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Efficient electrochemical oxidation of thallium (I) in groundwater using boron-doped diamond anode

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Abstract

Thallium (Tl) is a highly toxic element whose occurrence is widespread in soil and groundwater. The present study investigates the oxidation of Tl(I) with boron-doped diamond (BDD) anode in an electrochemical system, compared with PbO_2 and carbon felt materials. Under initial conditions of Tl(I) of 10 mg L^{-1}, pH of 2.0, and current density of 5 mA cm^{-2}, 99.2 ± 0.9% of Tl(I) is oxidized to Tl(III) within 15 min. This process is suppressed by the increase of initial Tl(I) concentration and initial pH, respectively, while it is enhanced with the increase of current density. Compared with direct electrochemical effect, indirect electrochemical oxidation with the generated oxidants mainly contribute to the excellent performance and ·OH plays a significant role. Subsequent coagulation/precipitation realizes the nearly complete

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removal of total Tl in the exhaust electrolyte and the quality of the effluent can meet EPA drinking water standards. Analysis of the generated precipitate further indicates that Tl(III) is the main oxidation state of Tl. This study offers a potentially attractive method for remediation of Tl-polluted groundwater.

Keywords: Thallium; Electrochemical oxidation; Boron-doped diamond anode; Groundwater

1. Introduction

Thallium (Tl), a bio-accumulative element, is commonly responsible for environmental contamination [1,2]. Compared with other heavy metals such as Pb, Ni and Zn, Tl is more toxic to mammals [3]. Though Tl and its compounds have many applications, including in fiber (optical) glass manufacture, and as semiconductors and lasers, fireworks, pigments and dyes [4,5], its excessive discharge is hazardous to the eco-system and human health [6]. It enters soil and groundwater primarily through metal-based mining, ore processing, smelting, and coal combustion. Ingestion of Tl causes both chronic and acute poisoning [7,8]. There are two main oxidation states of Tl, i.e. monovalent (Tl(I)) and trivalent (Tl(III)) cations, while the former is more widespread in the natural environment and of stronger mobility than the latter [9]. Oxidation of Tl(I) facilitates Tl removal from environment. Over the past few years, several different technologies have been employed for Tl removal, among which adsorption is frequently employed [10-13], whereas it requires large amounts of adsorbents which are very expensive and difficult to regeneration or disposal. Thus a

simple, efficient way of treating Tl-contaminated groundwater is urgently needed.

Nowadays, electrochemical oxidation technology is considered a green, efficient method for the removal of contaminants from soil and water, owing to the strong oxidative oxidants produced during electrolysis [14,15]. To date, electrochemical process has been widely used for remediation of metal-contaminated aqueous systems, with various metals as targets, including As, Pb, V, Cd [16-18], while few contributions are focused on Tl removal based on this technology. Additionally, anode materials, which determine the removal efficiency of target pollutants, are particularly important for the performance of electrochemical oxidation technology [19,20]. The boron-doped diamond (BDD) anode has become increasingly the electrode of choice in electrochemistry, noting its unique advantage in the complete mineralization of organic pollutants [21-23]. To date, hardly any investigations have been made into the treatment of Tl-contaminated groundwater with this particularly efficient electrode.

The present study proposed an electrochemical oxidation system with a BDD anode for the effective oxidation of Tl(I) in simulated groundwater. A systematic program of tests was undertaken to enable selection of suitable material for the anode, with removal efficiency in mind. Operating factors affecting the performance as well as possible oxidation mechanisms were also examined. Exhausted electrolytes were subjected to subsequent coagulation/precipitation tests; and the precipitate was further analyzed. This work provided a promising alternative for treating Tl-contaminated groundwater.

2. Methods and Materials

2.1 Experimental apparatus and chemicals

The configuration of the proposed system consisted of a power supply and an electrolytic reactor with copper wires connected together during the experiment (Fig. 1). The electrolytic reactor was fabricated from a glass beaker (250 mL) whose working volume was 200 mL. The BDD electrode with surface area of 5 cm^2, provided by CONDIAS GmbH, Germany served as anode. Other two kinds of anode materials, PbO_2, and carbon felt, prepared according to Li et al. [19], were also tested. The cathode was made of graphite plate with surface area of 10 cm^2 during all the experiments. The electrode spacing was 1.0 cm during the experiments [24]. Freshly prepared solution with Tl(I) concentration of 10 mg L^{-1} was added to the reactors, in the form of $TlNO_3$, and its initial pH was adjusted to 2.0 by 0.1 M HCl. All other chemicals were of analytical grade and utilized without further purification.

2.2 Experimental procedures

The oxidation of Tl(I) with initial concentration of 10 mg L^{-1} was conducted in the electrochemical system with a current density of 5 mA cm^{-2} within 15 min operating cycle. The performance of BDD anode was comparatively evaluated with PbO_2 and carbon felt anodes in the aspect of Tl(I) oxidation, by measuring the production of Tl(III) as the generated Tl(III) was soluble under this condition. Subsequently influencing factors affecting the performance of the system were examined, including initial Tl(I) concentration (5 mg L^{-1}, 10 mg L^{-1}, 15 mg L^{-1}, 20 mg L^{-1}), initial pH (1.5, 2.0, 2.5, 3.0) and current density (1 mA cm^{-2}, 5 mA cm^{-2}, 10 mA cm^{-2}, 15 mA cm^{-2}). When one factor was examined, it changed while others kept

consistent with the condition in the first part of the experiment. The initial pH was adjusted by 0.1 M HCl. After that, the oxidation process and its underlying mechanism were investigated through electrochemical test and by synchronous monitoring of active substances and the oxidation products. Subsequent coagulation/precipitation with the exhausted electrolyte by two different coagulants was performed to remove total Tl from the aqueous solution, i.e. addition of 2.5 g of ferric chloride ($FeCl_3 \cdot 6H_2O$) or polymeric ferric sulfate (PFS) respectively with magnetic stirring and pH of 9.0 by 1 M NaOH. Then the solution was filtered through a suction filter with 0.22 μm membrane. Tl(III) and total Tl were examined in the filtrate and the generated precipitate during that process was then analyzed using X-ray photoelectron spectroscopy (XPS). All experiments were carried out at room temperature (22 ± 2 ºC). Each test was repeated three times and the mean results were reported.

2.3 Analytical methods

The concentration of Tl(III) was measured by a UV-vis spectrophotometer (DR 5000, HACH, USA) at 605 nm [25]. Total Tl was determined by graphite furnace atomic absorption spectrophotometry (Zeenit700, Analytik Jena AG, Germany). pH was measured using a pH-201 meter (Hanna, Italy). Cycle voltammetry (CV) was performed at a scan rate of 50 mV s^{-1} using an electrochemical workstation (VMP3, Bio-Logic Science Instruments, France) with saturated calomel electrode (SCE) as reference electrode [26]. The concentration of total oxidizing species were monitored by N,N-diethyl-p-phenylenediamine (DPD) colorimetric method [27]. The

concentration of hydrogen peroxide was also measured by the spectrophotometer (DR 5000, HACH, USA) at 350 nm, after the sample was mixed with 0.01 M ammonium heptamolybdate tetrahydrate and 0.1 M potassium iodide [24,28]. Hydroxyl radical was determined using dimethyl sulfoxide (DMSO) [27,29]. Element composition of the precipitate was analyzed by XPS (AXIS-Ultra, Kratos Analytical, UK).

On the basis of measured Tl(III), current efficiency (CE) was calculated using the following equation:

$$CE = \frac{[Tl(III)_t - Tl(III)_0]FV}{120It} \quad (1)$$

where $Tl(III)_0$ and $Tl(III)_t$ are the concentration of Tl(III) (in g L^{-1}) at time 0 and t (in s), respectively; F is Faraday constant (96 487 C mol^{-1}); V is the volume of electrolyte (in L); I is the current (in A).

3. Results and Discussion

3.1 Tl(I) oxidation behaviors with BDD anode

Obvious Tl(I) removal was observed in the electrochemical system equipped with BDD anode, under the initial conditions of Tl(I) of 10 mg L^{-1}, pH of 2.0, and current density of 5 mA cm^{-2}, as shown in Fig. 2a. Tl(I) removal efficiency reached as high as 99.2 ± 0.9% within 15 min operation, which represented a major improvement on previous adsorption studies for Tl(I) using modified *Aspergillus niger* biomass [30] and nano-sized manganese dioxide [31] with the same initial Tl(I) concentration. The CE for the oxidation of Tl(I) with BDD anode was about 7.1 ± 0.4%, comparable with previous results using the same anode material [32]. Comparatively, Tl(I) removal

efficiencies achieved using the PbO_2 and carbon felt anode materials were 30 ± 1.1% and 11.3 ± 0.8%, respectively, much lower than that obtained from BDD anode, implying that electrochemical oxidation with BDD anode was efficient for Tl(I) removal in groundwater.

Compared with the other two anode materials, BDD electrodes exhibited high oxygen over-potentials when producing electrochemical oxidants in situ from water, and the oxidants were short-lived free radical species such as ·OH, O·, HO_2· [33] and more stable substances such as H_2O_2, O_3, $S_2O_8^{2-}$, ClO^-， HClO [34-36]. BDD anodes had previously been classified as non-active anodes having a weak interaction between the anode surface and electro-generated hydroxyl radical [26,37,38]. Therefore, once hydroxyl radicals formed during the reaction procedure, they would then fall from the BDD anode surface into the solution and so Tl(I) was rapidly oxidized to Tl(III) [39,40]. In contrast with the BDD case, the hydroxyl radical remained attached to the PbO_2 electrode surface in an adsorbed state because of the strong adsorption properties of the electrode material [41], and thus such radicals hardly entered the solution. Far fewer hydroxyl radicals formed on the carbon felt electrode than on the other two electrodes. In short, the main advantages of BDD electrodes were their relatively wide electrochemical potential window, chemical inertness and thermal properties, and their stability under polarity inversion [36,42].

Four gradients of initial Tl(I) concentration were examined and Tl(I) removal efficiencies decreased gradually with the increase of initial Tl(I) concentrations (Fig. 2b). After 15 min operating, Tl(I) was nearly completely removed when initial Tl(I)

concentrations were 5 mg L^{-1} and 10 mg L^{-1}. When they were increased to 15 mg L^{-1} and 20 mg L^{-1}, the removal efficiency decreased to 76.4 ± 1.2% and 62.8 ± 0.9%, respectively. The amount of active substances generated in the system might be constant, so as the Tl(I) that could be oxidized. Thus proper range of initial Tl(I) concentrations with corresponding operating time should be chosen to ensure the quality of groundwater after treatment in the proposed system.

Fig. 2c illustrated that the removal efficiency of Tl(I) decreased with the increase of initial pH. Notably, increasing the pH from 2.5 to 3.0 resulted in the significant decrease of Tl(I) removal. Acidic condition facilitated the formation of oxygen containing active substances, which could be propitious to oxidation process [43,44]. Moreover, the adjustment of pH by HCl was also an important factor, as the addition of chloride ion could easily form complex compounds with the generated Tl(III), which was favorable to the oxidation of Tl(I) [45]. Additionally, chlorion-related intermediate could also be generated during the electrolysis process, accelerating the oxidation of Tl(I) during the test. Therefore, the removal efficiency of Tl(I) decreased with the increase of pH due to the lack of hydrogen and chloride ions.

It could be seen from Fig. 2d that the efficiency of Tl(I) removal increased gradually with the increase of current density. Higher current density could result in stronger direct electrochemical oxidation, and more active substances could also be produced, both of which could promote the removal of Tl(I) [46]. Though higher current density the results achieved more quick Tl(I) removal, more energy would be consumed. Appropriate current density should be selected for economical

consideration.

3.2 Tl(I) oxidation mechanisms

The two main electrochemical oxidation mechanisms comprised: (1) direct electrochemical effects on the anode surface; and (2) indirect electrochemical effects mediated by oxidants, such as hydroxyl radicals, hydrogen peroxide and active chlorine generated during electrolysis [41,47]. The oxidation peaks in the CV with BDD anode got weaker and weaker as the experiment progressed (Fig. 3) [26], while the oxidation efficiency of Tl(I) increased during the experiments (Fig. 2a), implying that the direct electrochemical oxidation was not the main effect for Tl(I) removal, consistent with previous studies [48,49]. The hydrogen peroxide and hydroxyl radicals were subject to further monitoring and both of them exhibited an increasing tendency with time (Fig. 4), and so as the total oxidizing species with the maximum value of 9.51 ± 1.3 mg L^{-1} and the concentration level was comparable with results obtained from the exact system for treating *p*-substituted phenols [41]. This result suggested that indirect oxidation pathway by oxidants generated in electrochemical tests played a more important role for Tl(I) removal.

The main oxidants, hydrogen peroxide and hydroxyl radical, were generated as follows: (i) oxygen captured electrons on the cathode readily, and reacted with hydrogen ions to form hydrogen peroxide in the acid solution (Eq. (2)); (ii) hydroxyl radical formed due to single-electron oxidation of water because of the high voltage on the anode (Eq. (3)) [33,50]. Moreover, active chlorine, such as Cl_2 and HClO,

could also be generated due to the addition of chloride ion according to Eq. (4), (5) [46].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

$$H_2O \rightarrow \cdot OH + H^+ + e^- \quad (3)$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (4)$$

$$Cl_2 + H_2O \rightarrow HClO + HCl \quad (5)$$

To deeply investigate the exact roles of these active oxidative species during the electrolysis process, different oxidant scavengers were added into electrolyte at the beginning of tests according to previous studies [51,52]. Compared with the result without scavenger in Fig. 2a, addition of isopropanol to remove ·OH solely significantly inhibited the oxidation efficiency of Tl(I) (only about 8 ± 0.4%) (Fig. 5), suggesting that the Tl(I) oxidation pathway by ·OH was dominant, which coincided with previous study [49]. While with the addition of $FeSO_4$-EDTA solely to remove H_2O_2, the oxidation efficiency decreased slightly (about 86 ± 1.5%), indicating H_2O_2 played a less significant role. Results from additions of both ·OH and H_2O_2 scavengers simultaneously indicated that the effect of active chlorine (Cl_2, HClO) could be negligible [53]. Although some chemical reaction, for instance Fenton reaction, could also produce oxidants as ·OH, other chemical reagents must be added into the aqueous solution, probably resulting in higher cost and secondary pollution [54].

With the aids of these oxidants, Tl(I) was oxidized satisfactorily to Tl(III) in a current density of 5 mA cm^{-2} (Eq. (6), (7), (8), (9)) . The concentration of Tl(III)

increased accordingly as presented in Fig. 2a.

$$Tl^{+} + H_2O_2 + 4Cl^{-} + 2H^{+} \rightarrow TlCl_4^{-} + 2H_2O \quad (6)$$

$$Tl^{+} + 2{\cdot}OH + 4Cl^{-} + 2H^{+} \rightarrow TlCl_4^{-} + 2H_2O \quad (7)$$

$$Tl^{+} + 2Cl_2 + 2e^{-} \rightarrow TlCl_4^{-} \quad (8)$$

$$Tl^{+} + 4HClO + 4H^{+} + 6e^{-} \rightarrow TlCl_4^{-} + 4H_2O \quad (9)$$

Additionally, the importance of HCl in achieving full removal of Tl(I) was highlighted as the generated Tl(III) strongly binded to unidentate ligands with Cl^{-} to form stable charged anionic species $TlCl_4^{-}$, which was the main final product of Tl(III) [55,56]. Given that the pairing of Tl(III) and Tl(I) had high redox potential (+1.25 V), Tl(I) could, in principle, be easily oxidized to Tl(III) in acidic condition [45]. It should be noted that Tl(III) generally occurred in a strong oxidizing environment and was easily hydrolyzed in solution [31]. Therefore, the presence of chloride ion prevented Tl(III) from becoming hydrolyzed; this was a very satisfactory finding in the context of the present study as Tl(III) in the form of $TlCl_4^{-}$ could precipitate more readily than hydrolyzed on during coagulation/precipitation process [56]. As should be found from Fig. 2a, most generated Tl(III) was still in the aqueous solution and the concentration of total Tl kept steady after electrochemical treatment, with slight increase of pH (from 2.00 to 2.07), thus subsequent treatment was necessary to achieve total Tl removal and ensure groundwater security.

3.3 Subsequent treatment for total Tl removal

After electrolysis, subsequent treatment was performed for the exhausted electrolyte. When its pH was adjusted to 9.0, spontaneous precipitation was hardly observed as strongly steady $TlCl_4^-$ was the main form of Tl(III). It was tetrahedral with all the coordination sites of Tl(III) were fully occupied by chloride and hydroxyl ions lost the chance to combine with Tl(III) [57]. When the two coagulants were added separately, significant removals of total Tl were realized through the bridge formation and catching-sweeping mechanism in flocculating process (Fig. 6). The quality of the treated effluent could meet EPA drinking water standards (less than 2 μg L^{-1}) [58]. The foregoing results demonstrated that the proposed process i.e. oxidation in the electrolytic reactor and subsequent coagulation/precipitation was capable of remediation of Tl-polluted groundwater efficiently.

Precipitates from the coagulation/precipitation with different coagulants were further analyzed by XPS (Fig. 7a). The spectrum had a peak corresponding to Tl 4f and measured banding energy located at 118.2 eV, which could be ascribed to Tl(III) [59,60]. The high resolution of Tl 4f was shown in Fig. 7b, which indicated that about 99% and 92% of Tl(III) was removed from the solution in coagulation/precipitation with $FeCl_3$ and PFS, respectively. The lack of a peak corresponding to Tl(I) indicated that scarcely any Tl(I) remained in the precipitate. These results showed that Tl(I) was almost completely oxidized to Tl(III) and deposited on the $Fe(OH)_3$ surface. Moreover, the XPS spectrum also indicated the presence of O 1s and Fe 2p with the respective peaks located at approximately 531.1eV and 711.0 eV. Given that the two peaks correspond to nucleophilic oxygen (O^{2-}) and Fe^{3+}, the oxides were inferred to

259 be Fe_2O_3, due to slow decomposition of the weak base ($Fe(OH)_3$) [61,62]. The
260 foregoing discussion had explained the chemistry of the processes behind Tl removal
261 using the technology presented herein.

262 **4. Conclusions**

263 99.2 ± 0.9% of Tl(I) was successfully oxidized to Tl(III) in the electrolytic
264 reactor with BDD anode within 15 min. Tl(I) oxidation was suppressed by the
265 increase of initial Tl(I) concentration and initial pH, respectively, while it was
266 enhanced with the increase of current density. Compared with direct electrochemical,
267 indirect oxidation reaction with ·OH played a significant role. Subsequent
268 coagulation/precipitation with $FeCl_3$ realized the satisfactory of total Tl removal and
269 the quality of the effluent could meet EPA drinking water standards. XPS analysis
270 further confirmed that Tl(III) was the primary oxidation state of Tl. An efficient
271 alternative had therefore been proposed for remediation of Tl-contaminated
272 groundwater.

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454 **Figure Captions**

455 **Fig. 1.** Schematic diagram of the electrolysis system used in the present study.

456 **Fig. 2.** The removal efficiency of Tl(I) with different anode materials (a) as well as
457 operating factors studies. (b) initial Tl(I) concentration; (c) initial pH; (d) current
458 density.

459 **Fig. 3.** CV curves with the BDD anode at the scan rate of 50 mV s^{-1}.

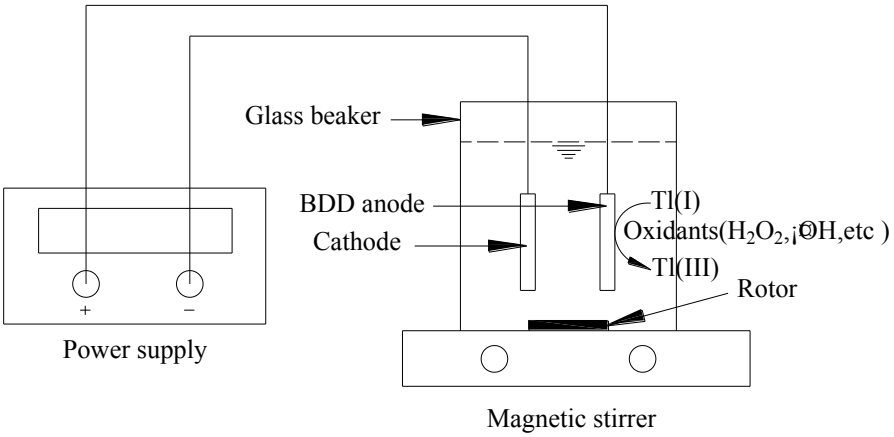
460 **Fig. 4.** Concentration evolution of hydrogen peroxide and hydroxyl radical produced
461 on BDD anode during the experiment.

462 **Fig. 5.** The oxidation efficiency of Tl(I) with different scavengers in the electrolytic
463 reactor.

464 **Fig. 6.** Histogram showing concentrations of total Tl and Tl(III) at initial conditions
465 for $FeCl_3$ and PFS used in the coagulant tests.

466 **Fig. 7.** XPS spectra for precipitate from the coagulant test with $FeCl_3$ and PFS: (a)
467 survey; and (b) high resolution plot in vicinity of Tl 4f.

468



469

470 **Figure 1**

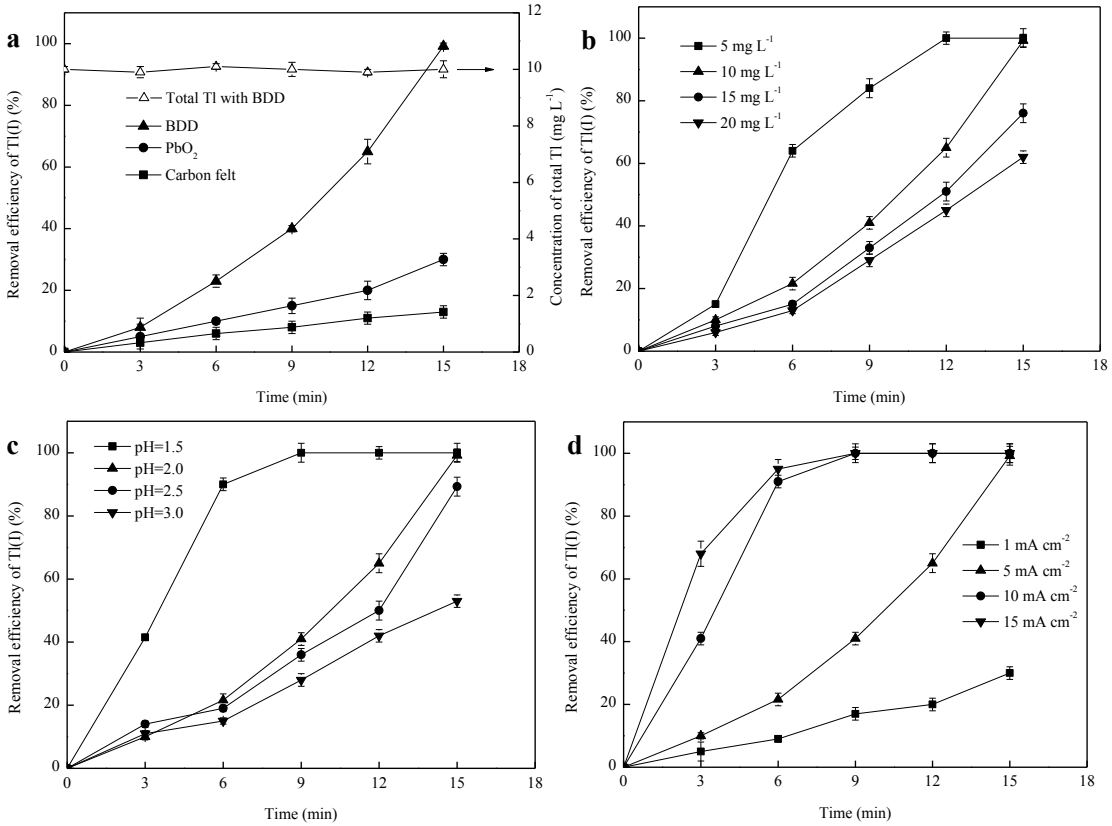
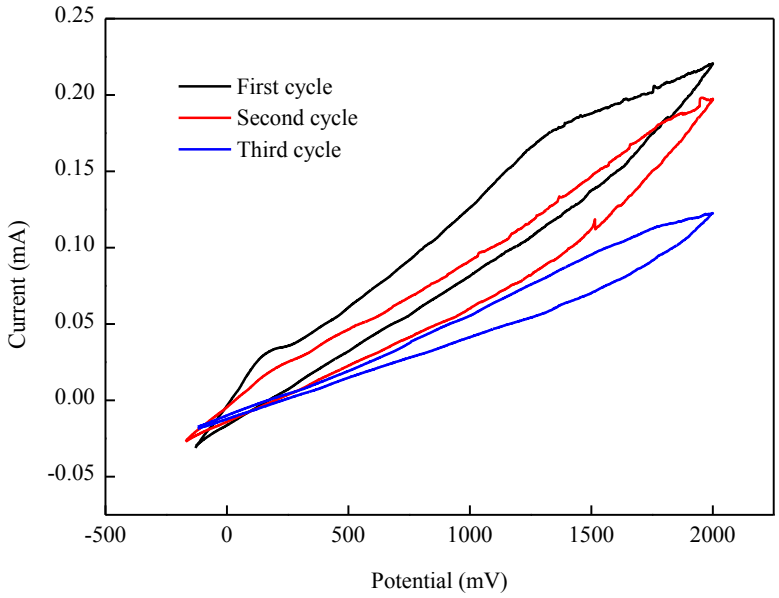

a
Removal efficiency of Tl(I) (%)
Concentration of total Tl (mg L-1)
Time (min)
Total Tl with BDD
BDD
PbO2
Carbon felt
b
Removal efficiency of Tl(I) (%)
Time (min)
5 mg L-1
10 mg L-1
15 mg L-1
20 mg L-1
c
Removal efficiency of Tl(I) (%)
Time (min)
pH=1.5
pH=2.0
pH=2.5
pH=3.0
d
Removal efficiency of Tl(I) (%)
Time (min)
1 mA cm-2
5 mA cm-2
10 mA cm-2
15 mA cm-2

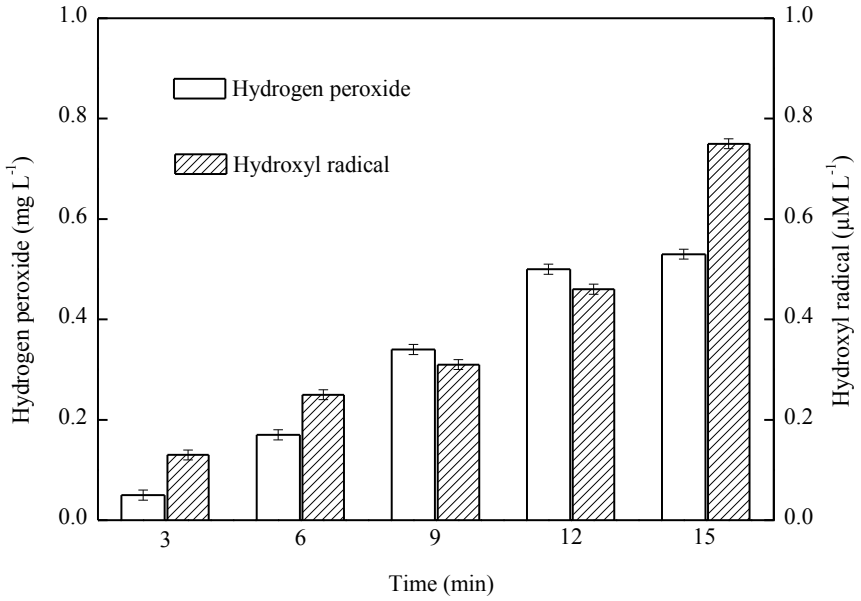
Figure 2



474

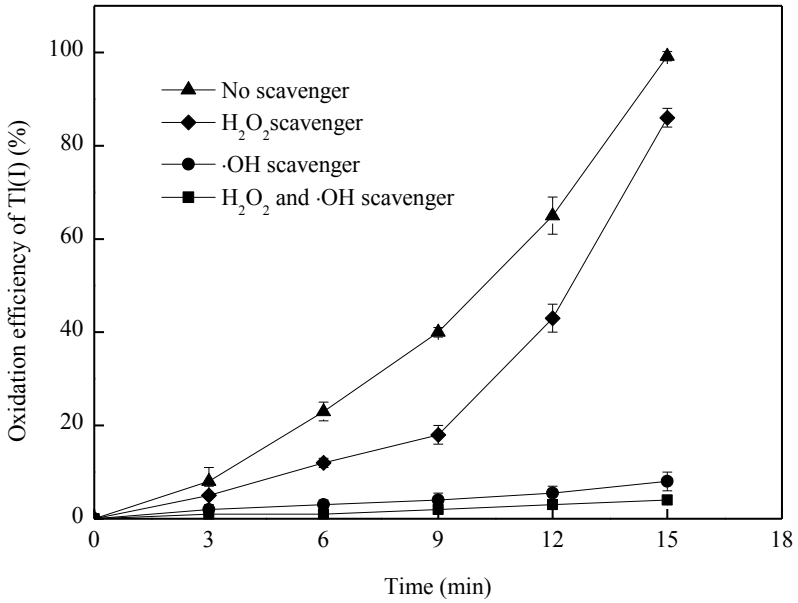
475 **Figure 3**

476



477

478 **Figure 4**



479

480 **Figure 5**

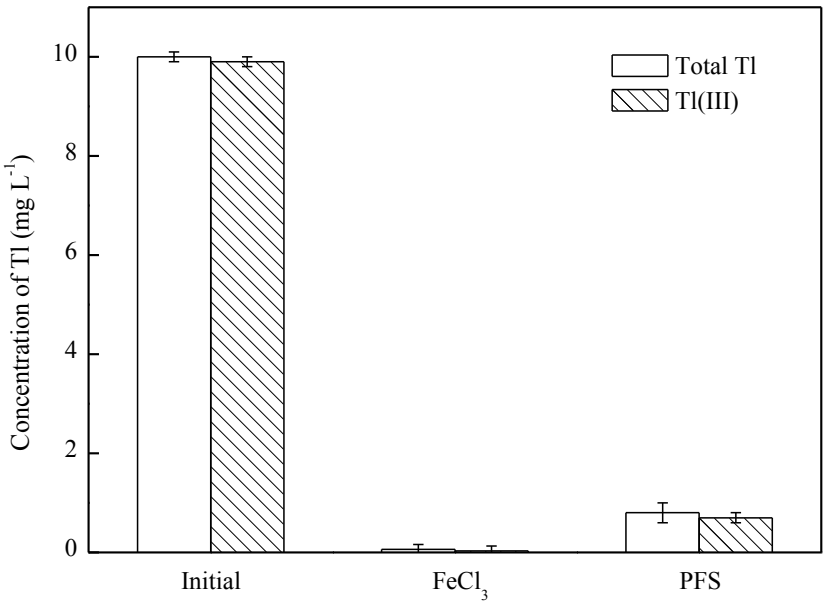
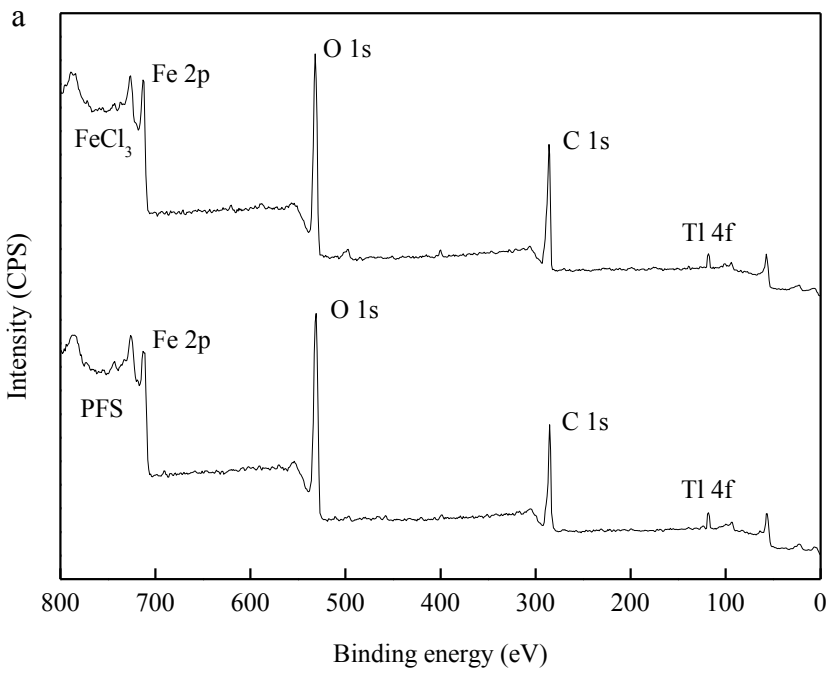

Concentration of Tl (mg L-1)
10
8
6
4
2
0
Total Tl
Tl(III)
Initial
FeCl3
PFS

Figure 6



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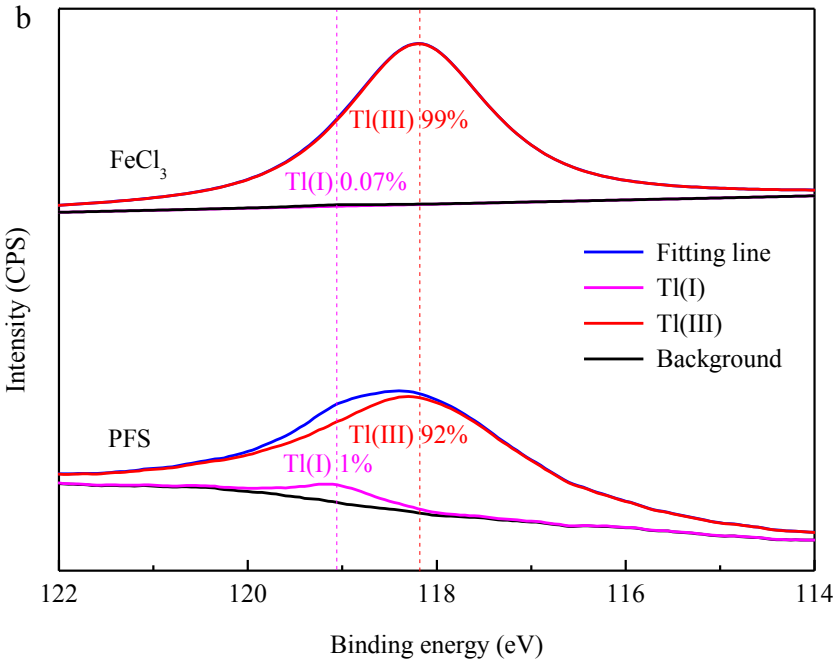

484

485 **Figure 7**